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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09B 67/46, C09D 17/00, B01F 17/44 — A1

(11) International Publication Number: WO 97/41178

(43) International Publication Date: 6 November 1997 (06.11.97)

(21) International Application Number: PCT/US97/07704

(22) International Filing Date: 23 April 1997 (23.04.97)

(30) Priority Data:
60/016,716 2 May 1996 (02.05.96) US

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(81) Designated States: AU, BR, CA, CN, IL, JP, KR, MX, NZ, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: AQUEOUS DISPERSIONS CONTAINING SUBSTITUTED SUCCINIC ANHYDRIDE DERIVATIVES

(57) Abstract

Aqueous dispersions of solids and dispersing agents which are derivatives of substituted succinic acids are disclosed. Methods of making and using such dispersions are also disclosed.

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AQUEOUS DISPERSIONS CONTAINING SUBSTITUTED SUCCINIC ANHYDRIDE DERIVATIVES

Field of the Invention

This invention relates to dispersions of a solid, particularly a dyestuff or a pigment, in an aqueous medium containing as a dispersing agent, a substituted succinic anhydride derivative.

Background of the Invention

Derivatives of substituted succinic anhydrides are described in the art. Compounds which are derived from alkenyl succinic anhydrides having C_6 to C_{22} alk(en)yl groups and/or substituents of functional groups elsewhere in the molecule are described in PCT Pub. No. WO94/00508, published January 6,1994, as having significant surfactant properties. In particular, they are described as performing well as non-ionic surfactants, particularly in aqueous systems, and as having unexpected cloud point properties indicating good performance at elevated temperatures and activity under alkaline conditions. Also the surfactants are described as having good biodegradation properties.

These compounds are described as having emulsification properties and wetting and dispersion capabilities. These include generally use in oil in water emulsions for metal working fluids, based on semi-soluble oil and synthetics and for crude oil transportation and fuel systems; emollients for personal (skin) care; domestic detergent compositions, for example, laundry liquids; dispersions of organic and inorganic powders in paints and coatings (e.g. filler and pigments); agrochemical formulations (e.g. pesticides); wetters in industrial and institutional cleaning products (e.g. traffic film removers, bottle washes). The compounds are particularly described as suitable for wool scouring and as inverting agents in the manufacture of acrylamide.

Dispersing agents which are particularly suitable in the preparation of dispersions of solids, particularly dyestuffs and pigments, in organic liquids are described in United States Patents 4,224,212 and 4,861,380, which are incorporated herein by reference.

However, there remains an unfulfilled need in the art for dispersing agents which are capable of and suitable for forming dispersions of a solid in an aqueous medium. Further, there is a continuing need in the art for dispersing agents which form dispersions which possess low viscosity and high stability with pigments present in a high concentration.

Summary of the Invention

The present invention advantageously and surprisingly fulfills the above-described needs. In accordance with the present invention, compounds which are particularly effective as dispersing agents for a solid in an aqueous medium have been advantageously discovered. Accordingly, the present invention provides an aqueous dispersion of a solid and a dispersing agent, which agent is defined by the following formula I.

The dispersing agents used in the dispersions of the present invention are compounds of the structure:

$$Y.O_2C.(HR)C.C.(HR^1).CO_2.(C_mH_{2m}O)_n.R^2 \quad (I)$$

wherein

one of R and R^1 is C_{14} to C_{22} alkyl or alkenyl and the other is hydrogen;

n is from about 4 to about 200 (and as it is an average, it may be non-integral);

m is 2, 3 or 4 (and may vary along the polyoxyalkylene chain);

R^2 is hydrogen or C_1 to C_{22} hydrocarbyl, particularly alkyl; and

Y is hydrogen, a metal, particularly an alkali metal, ammonium, or amine onium, especially alkylamine (including alkanolamine), C_1 to C_{22} hydrocarbyl, particularly alkyl, or a group of the formula $(C_mH_{2m}O)_n.R^2$, where m, n and R^2 are independently as defined above.

The solid may be any inorganic or organic compound which is substantially insoluble in the aqueous medium.

The present invention is advantageously and particularly useful for providing aqueous dispersions of a solid, which is a pigment or a dyestuff.

These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description and appended claims.

Detailed Description of the Invention

As indicated above, the aqueous dispersions of the present invention contain a dispersing agent and a solid. Each of these is described separately below.

Dispersing Agent

The dispersing agents employed in the dispersions of the present invention are represented by the above formula (I).

The following particular sub-group of compounds of formula (I) are particularly useful within the scope of the invention:

$$Y.O_2C.(HR)C.C(HR^1).CO_2.(C_mH_{2m}O)_n.R^2 \qquad \text{(Ia)}$$

wherein R, R^1, R^2, m and n are as defined above for formula (I) and Y is a C_1-C_{22} hydrocarbyl, particularly alkyl, group.

The group Y can be hydrogen, a metal, particularly an alkali metal, ammonium, or amine onium, especially alkylamine (including alkanolamine),

or a C_1 to C_{22} hydrocarbyl particularly alkyl, group, or a group of the formula $(C_mH_{2m}O)_n.R^2$, where m, n and R^2 are independently as defined for formula (I). Where Y is hydrogen, the compounds of the formula (I) include a free carboxyl group and this can readily be replaced by metal or onium groups by alteration of the pH of the medium.

The group R^2 is desirably either H or a C_1-C_{22} hydrocarbyl, particularly alkyl group. Where R^2 is H, the compounds tend to be relatively more hydrophilic, and where R^2 is an alkyl group, relatively less hydrophilic. The choice of the group R^2 can be determined based on the desired overall properties of the compound.

Where the groups Y and/or R^2 are or include hydrocarbyl groups, they are particularly alkyl (or alkenyl) groups and can especially be lower alkyl groups, e.g., C_1 to C_6 alkyl such as methyl, ethyl, propyl, butyl, pentyl or hexyl (including branched propyl, butyl, pentyl and hexyl), acting as chain end cap(s) for the polyalkylene oxide(s) chain or as a second ester group, to alter the degree of hydrophilicity of the compounds, or longer chain alkyl or alkenyl groups, e.g., C_8 to C_{22} alkyl or alkenyl groups such as lauryl, oleyl and stearyl groups or mixed alk(en)yl groups derived from natural fats or oils or from distillation cuts in petrochemical synthesis, acting as secondary hydrophobe(s) in the molecule.

The compounds useful in the invention further include at least one polyoxyalkylene chain composed of residues of ethylene glycol ,and/or propylene glycol,and/or butylene glycol. The chain may be a homopolymer chain or a block or random copolymer chain containing two or all three kinds of glycol residues, usually including at least some ethylene glycol residues. In compounds including more than one polyoxyalkylene chain, the chains can be the same or different, as described above.

The polyoxyalkylene chain is defined as the group $(C_mH_{2m}O)_n$ in formula (I) (including Ia). The chain length of this group, i.e., the value of the parameter n, can be chosen to provide the desired properties for the compound. The longer the chain and the higher the proportion of ethylene glycol residues, the more hydrophilic the compound is. Typically, where the polyoxyalkylene chain is a polyoxyethylene chain, n generally ranges from about 4 to about 200, and particularly from about 10 to about 200, especially from about 15 to about 180. Where it is a polyoxypropylene or polyoxybutylene chain, n generally ranges from about 5 to about 50, and preferably from 10 to 30. Where the chain is a block or random copolymer of ethylene and/or propylene and/or butylene glycol residues, the chain length chosen will typically correspond to the above ranges, but numerically according to the proportion of ethylene and/or propylene and/or butylene glycol residues in the chain. Numerical values of the repeat length of the polyoxyalkylene chain are average values and can be non-integral. Where integral values are given, they will usually be approximate values.

It is contemplated that any molecular weight of polyethylene glycol (PEG), such that n of Formula I or (Ia) ranges from about 4 to about 200, is suitable for use in the compounds. Non-limiting examples of suitable PEGs include PEG 600, 1000, 1500, 2000, 4000, 5000, 6000 and 8000, and of PEG ethers, the corresponding (R^2) alkoxy PEGS, e.g., methoxy PEG 750, 2000 and 5000.

The compounds where the group R or R^1 is a C_{14} to C_{18} alkyl or alkenyl group are especially desirable and suitable for forming the dispersions of the present invention. More particularly, compounds, where the group R or R^1 is an alkenyl group, are preferable over those where the group is alkyl.

The compounds of formula (I) can be made by reacting an alkenyl or alkyl succinic anhydride with a compound of the formula: $H.O.(C_mH_{2m}O)_n.R^2$

(where m, n and R^2 are as defined above). The reaction between the anhydride and the polyalkylene glycol, or a polyalkylene glycol mono alkyl ether, can be readily carried out, with or without catalysts, by bringing the glycol into contact with the alkenyl or alkyl succinic anhydride. The reaction occurs typically at temperatures below about 200°C, and more typically below about 100°C. The reactants will usually be present in at least approximately stoichiometric proportions. Particularly where stoichiometric proportions are used, further purification does not usually appear to be necessary, but can be optionally carried out if desired.

The product of the reaction is typically a mixture of isomers corresponding to the two senses of the anhydride ring opening reaction. It has been noted that the alkenyl or alkyl chain seems to have a minor steric effect on the isomer ratio with the isomer ratio being typically about 60:40; the major isomer arising from nucleophilic attack at the anhydride carbonyl group remote from the alkenyl or alkyl group.

The product of the above reaction is an ester having a free carboxyl groups, i.e., Y is H. Compounds where Y is a metal or onium group can be made by reaction with corresponding bases at suitable pH. Compounds where Y is hydrocarbyl or $(C_mH_{2m}O)_n.R^2$ where m, n and R^2 are as defined for formula (I) above can be made by direct esterification of the carboxylic acid (Y=H) with the corresponding alcohol YOH or $HO(C_mH_{2m}O)_n.R^2$. The esterification of the free acid can be carried out in a conventional manner, for example, using an acid catalyst which may be sulphuric, toluene sulphonic, or phosphoric acid, or an alkyl titanate.

Alkenyl succinic anhydrides may be produced by reacting maleic anhydride preferably with an excess of an olefin having from 14 to 22 carbon atoms, particularly 14 to 18, for example, a 50 to 200% excess of olefin at a temperature in the range of from about 150 to 400°C and preferably from

about 180 to 250°C. The excess olefin is removed , for example, by distillation which is suitably carried out under vacuum. No catalyst is necessary, but it is preferred that an antioxidant be present. These anhydrides are well known commercial materials. With alkenyl succinic anhydrides prepared as described above, the double bond generally is at the 2-position of the alkenyl substituent.

To make compounds where the group R or R^1 is an alkyl group, either the unsaturated compounds can be hydrogenated or, preferably, the intermediate alkenyl succinic anhydride can be hydrogenated to yield an alkyl succinic anhydride. Typically, the hydrogenation is carried out in the presence of a hydrogenation catalyst such as Raney nickel or a Pd/C catalyst. Temperatures of from about 15 to 200°C and pressures of from about 0 to 200 bar absolute may be used and, if desired, a solvent may be present. For example, the hydrogenation reaction of an alkenyl succinic anhydride may be carried out at 100°C using 0.2% w/w of 5% Pd on C catalyst over a period of from 4 to 10 hours.

The dispersing compounds used in the present invention are readily made with low odor and, since polyalkylene glycols and polyalkylene glycol alkyl ether are readily transportable, can be made at locations distant from alkylkene oxide plants if they are used as reactants.

Solid

The solid may be any inorganic or organic compound which is substantially insoluble in an aqueous liquid at the temperature concerned and which is capable of comminution into a finely divided form. The invention is particularly directed to solids which are pigments or dyestuffs, and dispersions containing such solids are a particular aspect of the invention.

The term pigment includes both inorganic and organic pigments, as well as lakes and toners.

The pigment may be any substantially water-insoluble colorant which may be used for imparting color to a water-borne paint or ink. Such pigments are generally described in the Colour Index (Third Edition) and subsequent editions and appendices thereto, which are incorporated herein by reference. Preferred pigments are those which are conventionally used in water-borne paints and inks, such as copper phthalocyanines, carbon black, quinacridones, dianthraquinones, monoazo pigments, vat pigments, dioxazine violet, diketopyrrolopyrroles, titanium dioxides and iron oxides. The mean particle diameter of the finely-divided pigment particles is preferably <5 micrometers, and more preferably <1 micrometer.

As examples of organic pigments, these may include azo, thionindigo, anthraquinone, anthanthrone and isodibenzanthrone pigments, vat dye pigments, triphendioxazine pigments, phthalocyanine pigments, for example, copper phthalocyanine, its nuclear chlorinated derivatives and copper tetraphenyl or octaphenyl phthalocyanines, and other heterocyclic pigments, for example, linear quinacridone.

As examples of inorganic pigments, these may include chrome pigments including the chromates of lead, zinc, barium, and calcium and various mixtures and modifications, such as are commercially available as pigments of greenish-yellow to red shades under the names primrose, lemon, middle orange, scarlet and red chromes. Modified chrome pigments may contain, for example, sulphate radicals and/or additional metals such as aluminum, molybdenum and tin. Further examples of inorganic pigments are carbon black, titanium dioxide, zinc oxide, Prussian blue and its mixtures with chrome yellows which are known as Brunswick Greens or chrome greens, cadmium sulphide and sulphoselenide, iron oxides, vermilion and ultramarine.

These and various other pigments suitable for use in the present invention are described in Volume 2 of "Colour Index 2nd Edition," published jointly in 1956 by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colourists, under the heading of "Pigments" and in subsequent authorized amendments thereto, which is incorporated herein by reference.

The term "lake" denotes a water-insoluble metal salt or complex of an organic dyestuff which has been precipitated on a water-insoluble inorganic substrate such as alumina.

The term "toner" denotes a water-insoluble metal salt or complex, in particular a calcium or barium salt or complex, of a soluble or sparingly soluble organic dye-stuff, in particular an azo dyestuff, which has optionally been prepared in the presence of an extender such as rosin.

As specific examples of suitable lakes and toners, these may include the barium toner of-(2'-sulpho-4'-methyl-5'-chlorophenylazo)-2-hydroxy-3-naphthoic acid, the nickel complex of 3-(4'-chlorophenylazo)-quinoline-2:4-diol, the rosinated barium toner of 1-(2'-sulpho- 4'-chloro'5'-methylphenylazo) -2-naphthol, the aluminum lake of 1:4-dihydroxyanthraquinone- 2-sulphonic acid and a rosinated calcium toner of 1-(2'-sulpho-4'-methylphenylazo)-2-hydroxy-3-naphthoic acid.

Especially preferred pigments for use in the present dispersion are titanium dioxide, iron oxide, phthalocyanine blue and green, rubine toners, benzidine yellows and carbon blacks such as are used in publication gravure printing and newsprint ink.

As examples of suitable dyestuffs, these may include water-insoluble dyestuffs such as disperse dyestuffs. The dyestuffs may be, for example, azo dye-stuffs, such as monoazo and diazo dyestuffs and metallized derivatives

thereof, anthraquinone, nitro, phthalocyanine, methine, styryl, naphthoperinone, quinophthalone, diarylmethane, triarylmethane, xanthine, azine, oxazine and thiazine dyestuffs. If desired, the dyestuffs can be reactive dyestuffs which contain groups capable of forming covalent bonds with textile materials.

With respect to the dispersions of the present invention, any of the compounds within Formula I or (Ia) will form a satisfactory dispersion with a particular solid of interest. Optimization of conditions such as the ratio of dispersing agent to solid, the pH of the aqueous medium, and particle size of the solid, which are well within the skill in the art, may be carried out by routine experimentation to obtain the dispersions of the present invention.

The dispersions of the present invention can be obtained by any of the conventional and well known methods of preparing dispersions. Thus the solid, the aqueous liquid and the dispersing agent may be mixed together in any order and the mixture then subjected to a mechanical treatment to reduce the particle size of the solid, for example, by shaking, by ball milling, bead milling, gravel milling or plastic milling until the desired dispersion is formed.

Alternatively, the solid can be treated to reduce its particle size independently or in admixture with either the aqueous liquid or the dispersing agent, and the other ingredient or ingredients then added; following which, the dispersion can be obtained by stirring the mixture. A dispersion obtained in this manner and comprising the solid in finely divided form and one or more dispersing agents is a further feature of the invention.

The pH of the dispersions of the present invention typically range from about 7 to about 11.

The amount of dispersing agent present in the dispersion ranges from about 0.3% to about 40%, especially from about 0.5% to about 25%, based on the weight of the solid. The dispersion suitably contains from about 10 to

about 80%, especially from about 20 to about 65% by weight of the solid based on the total weight of the dispersion. One of skill in the art will readily recognize and appreciate that the amount of dispersing agent varies with the particle size of the solid. For instance, the finer the particle size of the solid, the more dispersing agent will be required to form the dispersions of the present invention. Such determinations can be readily ascertained by one of skill in the art without the exercise of undue experimentation.

The aqueous-based liquid or medium especially includes water, but it is contemplated that other aqueous media are suitable for practice of the present invention. These media include mixtures of water and liquid PEG ,e.g., PEG 200-600 at a concentration of about 1 to about 25%, particularly PEG 400 at about 5% in water. Any source of water can be utilized by one of skill in the art, if desired.

To avoid caking or hard sediment formation, one of skill in the art can add an amount of a typical anti-caking agent to the dispersion. See Outlines of Paint Technology by W.M. Morgan (1990), at pages 36 and 259, which are incorporated herein by reference. For instance, about 2 to about 10% by weight based on total pigment of $CaCO_3$ (Winnofil) can be added to prevent caking of the dispersion. Stearic acid is also suitable for increasing the volume of particles and reducing specific gravity, which results in the formation of soft and easily redispersed sediments.

If desired, one can add a suitable amount of an antifoaming agent, e.g., n-hexanol. Other suitable antifoaming agents are well-known to one of skill in the art, and are considered suitable, so long as there is no deleterious effect on the dispersions of the present invention.

The dispersions of the invention are fluid or semi-fluid compositions containing the solid in finely divided and usually deflocculated form, and can be used for any purpose for which dispersions are conventionally used.

Where the dispersions are semi-fluid, fluidity may be enhanced by the addition of fluidizing agents which are well-known in the art. Thus the pigment dispersions of the present invention can be utilized in the manufacture of printing inks, particularly publication gravure and newsprint inks, by incorporating the dispersions with the other components conventionally used in the manufacture of such inks. These dispersions are also particularly well-suited in the manufacture of paints and coatings, for which purpose the dispersions are incorporated into conventional resins. Inks and paints containing such dispersions are therefore further particular features of the present invention.

The dyestuff dispersions are useful in the preparation of textile printing inks or solvent dyeing systems and particularly where the dyestuff is a sublimable disperse dyestuff for transfer printing.

A further aspect of the present invention is a dispersion of a finely-divided pigment in a composition comprising water, one or more water-compatible resins and, as dispersant, one of the compounds described hereinbefore.

The water-compatible resin may be any water-soluble or water-insoluble polymer or a mixture thereof. However, it is preferred that the resin is water-insoluble because such resins have generally been found to provide paints or inks having better durability than water-soluble resin.

Example of suitable resins are acrylic, styrene-acrylic, polyester, polyurethane, acrylic-polyurethane, vinyl acetate, vinyl chloride polymers and co-polymers and water-dispersible alkyd resins. Preferred resins are acrylic, styrene-acrylic, polyester, polyurethane, and acrylic-polyurethane resins.

As already indicated, the dispersion of the present invention is suitable as a mill-base for the preparation of a water-borne paints and inks by admixture with water-compatible resin(s) and/or water and other ingredients

which are conventionally incorporated into water-borne paints and inks, such as preservatives, stabilizers, antifoaming agents and coalescing agents. Water-borne paints and inks comprising a dispersion according to the present invention are a further particular feature of the present invention.

It has been found that the present invention advantageously allows the preparation of high pigment content mill-bases with good fluidity (low viscosity) which can be used to prepare water-borne paints or inks with particularly useful properties with respect to durability, gloss and moisture resistance of the paint or ink films after application and drying of the paint or ink, compared with conventional paints and inks.

The present dispersant allows the preparation of superior paints and inks in terms of gloss and foam resistance when compared with other dispersants of equivalent HLB value and in terms of gloss and durability when compared with water-soluble dispersing resins.

Mill-bases for water-borne paints and inks are conventionally prepared by subjecting an aqueous dispersion of a pigment and one or more resins to a grinding operation in order to ensure that the pigment is finely divided and evenly distributed throughout the aqueous resin medium. Although the resin or resins used should be water-compatible, it is recognized that for optimum paint or ink (especially packaging ink) performance (especially durability), the resins used are preferably not water-soluble. Suitable water-insoluble resins may commonly be described as being water dilutable, water dispersible, or emulsifiable. However, it has been found that water-insoluble resins do not generally provide sufficient dispersing power to ensure adequate dispersion of the pigment, and it is therefore common practice to include water-soluble resins (which generally provide better dispersing power than insoluble resins) in such mill-bases with a consequent adverse effect on the performance of the derived paint or ink. It has now been found possible to provide mill-bases

with well-dispersed pigments by the use of dispersing agents of the present invention. The present invention thus permits the preparation of well-dispersed mill-bases containing water, water-insoluble resins, pigment and dispersing agent and little or no water-soluble resin. Surprisingly, the dispersing agent does not have an adverse effect on the performance of the paint or ink in the same way as does the water-soluble resin.

The dispersion can therefore be prepared by any of the methods used for the preparation of mill-bases provided that all the components, as hereinbefore defined, are included. Thus, for example, the resin or resins may be dispersed and/or dissolved in water. The dispersing agent and pigment, in a coarse or unmilled condition in which the mean particle diameter of the pigment is preferably >5 micrometers, more especially >10 micrometers, may then be added to the mixture. The mixture can then be submitted to a high-shear treatment, e.g. bead or ball milling, in order to produce an even dispersion of finely-divided pigment in the aqueous medium. A pre mill-base comprising a suspension of unmilled pigment in water containing the water-compatible resin and the dispersant is a further feature of the present invention.

A further advantage of the present invention is that the dispersion has improved wetting properties, reduced tendency to foam which makes milling and handling more convenient, and avoids or minimizes the need for antifoams, which are known to have a deleterious effect on paint or ink performance, in the mill-base. It also allows a reduction in, or avoidance of, the use of water-soluble resins which have an adverse effect on the durability and/or moisture resistance of the resultant paint or ink film.

The following examples are provided for purposes of illustrating the invention and should not be construed in any manner whatsoever as limiting

the scope of the present invention. All parts and percentages are by weight unless otherwise stated.

In the Examples, the following procedures and materials were employed:

Dispersion Preparation of Pigments A), B), and C)

Dispersions were made consisting of: (% W/W)

*) On dry pigment

(**) Foam control

The method used to make dispersions (100 g) was as follows. The calculated amount of dispersing agent was added to a 250 ml glass bottle, to which was then added demineralised water and n-hexanol. The components were then gently mixed to bring the dispersing agent into solution. Glass beads (3 mm diameter) were added (1/2 of the mill-base). The appropriate amount of pigment was then added and the dispersion was prepared by shaking in a Red Devil Lab shaker. Inorganic pigments were shaken for 1/2 hr. and organic pigments were shaken for 1 hr. Measurement of dispersion viscosity was carried out at low - shear rate (6 RPM) with a Brookfield LVT.

The following compounds were tested as dispersing agents:

Compd No	R/R1	R2	Y	n	m
1	C_{18} alkenyl	methyl	methyl	45	2
2	C_{18} alkenyl	methyl	butyl	45	2
3	C_{18} alkenyl	methyl	H	114	2
4	C_{14} alkenyl	H	H	22	2
5	C_{18} alkenyl	H	H	12	2
6	C_{18} alkenyl	H	H	22	2
7	C_{18} alkenyl	H	H	45	2
8	C_{18} alkenyl	methyl	H	45	2

The following pigments were tested with the above dispersing agents in the formation of aqueous dispersions.

A) Inorganics

GRADE	SUPPLIER	CHARACTERISTICS
Titanium dioxide		
Tioxide-TR92	Tioxide	White R2: rutile 94% TiO_2 Al, Zr coated + organic treatment
Kronos 2190	Kronos	White R2: rutile Al (3%), Zr (0.2%) coated
Iron Oxide (Red)		
Bayferrox 130M	Bayer	C.I. pigment red 101 95-97% Fe_2O_3 Al and Si coated (2-4%)

B) Organics

GRADE	SUPPLIER	CHARACTERISTICS
Phthalocyanine		
Monastral Blue FGX	Zeneca	C.I. Pigment Blue 15:4 (B)
Monastral Green GNX-C	Zeneca	C.I. Pigment Green 7

C) Carbon black

Elftex 120	Cabot	Furnace Black C.I. Pigment Black 7

D) General Purpose organic blue pigment (Miles Palomar Blue)

The basic formulation used for Examples 15-19 is described below:

Pigment	10g
Water	25g
Diethylene glycol	5g
Dispersant	2.5g
Lexorez 1100	2.5g

E) Auto Grade organic magenta pigment from Ciba Geigy Co.

The control formulation was comprised of pigment (29.3g), Acrysol I-62 (Rohm and Haas Co., 60g) and water (137g).

Method of Preparation of Samples with Formulations D and E

D) General purpose organic blue pigment.

Examples 15-19 were prepared on a standard Red Devil Shaker/mixer for 1 hour with 60 ml of ceramic beads (mean particle size 1.6-2.5mm SEPP Industries, Maple Heights, Ohio). The ceramic beads were strained with a standard paint filter to give the final dispersion.

E) Auto grade organic magenta pigment.

Examples 20 and 21 were prepared on an attritor (Reeves 1400ml capacity, a type of stirred bead mill) at 500rpm for 16 hours at ambient temperature (ambient temperature cooling water was used in the jacket). The dispersion was strained from the dispersion and then mixed into the Glidden Semi Gloss paint (1/4 ratio) and examined for color development.

The dispersions were also examined for transparency, a clarity test which measures the fineness of the dispersion, and particularly used by the auto industry. This test is run on the undiluted dispersion.

Color Development and Transparency Dispersion Tests

Sample Preparation

The filtered dispersion was mixed into a Glidden Semi Gloss white paint at a 1/4 wt. ratio.

A 3 mil (0.0762 mm) wet film (draw down) of this blue paint (Byk Gardner, Bird Applicator) was then applied to standard opacity cards (Leneta Co, form 9A), allowed to dry overnight and the color development measured as described below.

Three basic types of dispersion tests were carried out as follows:

1) "Rub up test"

This test is well known in the paint industry and is an indication of the degree of dispersion. After the drawdown was allowed to dry, the film was rubbed gently with the forefinger in a circular motion. If the dispersion was incomplete or flocculated, this motion further dispersed the system and the "rub up" area appeared a more intense color than the main body. All of the dispersions tested in Examples 15-21 passed this test.

2) Color Development or Relative Color Strength Test.

This test is the most widely used paint industry test to estimate the degree of dispersion. In the paint drawdowns described previously, the control was "drawn down" next to the experimental dispersion. The two films were allowed to dry and the "color development" or the intensity of the color of the films visually compared. The better dispersion exhibited a more intense color which, in these tests, was rated on a scale of 1 (poor) to 10 (excellent).

3) Transparency

This test is most often used in test dispersions for auto uses. The dispersion of the pigment was tested before being mixed with the white paint. Drawdowns were prepared on a transparent Melinex film, allowed to dry and examined visually for transparency. The dispersion was then judged by the clarity of the films.

EXAMPLES

Using the dispersing agent and pigment identified below, the following results were obtained.

Table 1: Titanium Dioxide Viscosity (mPa.s) of 65% in water

Dispersant concentration: % w/w on pigment

Example No	Compound No	pH	TIOXIDE TR-92			KRONOS 2190		
			0.5%	0.8%	1.1%	0.5%	0.8%	1.1%
1	1	7	9800	7000	6240	10760	2960	2500
2	1	10.2	1340	1220	1470	-	-	-
3	2	7	-	2180	1470	9360	1030	940
4	3	7	63	78	1400	16	16	16
5	3	10.2	1170	1400	1480	-	-	-

Table 2: Iron Oxide Viscosity (mPa.s) of 65% Bayferrox 130M in water

Dispersant concentration: % w/w on pigment

Example No	Compound No	pH	BAYFERROX 130M		
			0.5%	0.8%	1.1%
6	1	7	16	16	16
7	2	7	31	16	16
8	3	7	16	16	16

Table 3: Carbon Black Viscosity (mPa.s) of 30% w/w in water

Dispersant concentration: % w/w on pigment

Example No	Compound No	pH	ELFTEX 120	
			4%	6%
9	1	7	-	31.2
10	3	11	-	16

Table 4: Phthalocyanine Blue Viscosity (mPa.s) of 40% w/w in water

Dispersant concentration: % w/w on pigment

Example No	Compound No	pH	MONASTRAL BLUE FXG	
			4%	5%
11	3	7	1150	765
12	3	10.2	-	90

Table 5: Phthalocyanine Green Viscosity (mPa.s) of 40% w/w in water

Dispersant concentration: % w/w on pigment

Example No	Compound No	pH	MONASTRAL GREEN GNX-C	
			4%	5%
13	3	7	109	16
14	3	10	-	62

Table 6: Dispersion of phthalocyanine blue

Examples 15-19		15	16	17	18	19	
Composition (parts by weight)							
Pigment	10	10	10	10	10	10	10
D/DI Water	25	25	25	25	25	25	25
Diethylene glycol	5	5	5	5	5	5	5
IL 2678	5	-	-	-	-	-	-
Lexorez 1100 (2)	-	-	2.5	2.5	2.5	2.5	2.5
Compound 4	-	2.5	-	-	-	-	-
Compound 5	-	-	2.5	-	-	-	-
Compound 6	-	-	-	2.5	-	-	-
Compound 7	-	-	-	-	2.5	-	-
Compound 8	-	-	-	-	-	2.5	-
Test Results							
Color Development (1)	10	10+	10+	10	9	8	3

1) Visual rating - 10 excellent
(2) Diethyleneglycol adipate

Table 7: Dispersion of Auto(Ciba magenta) formulation

Examples 20-21	Control-1	Control-2	20	21
Composition (pts by wt)				
Pigment	29.3	29.3	29.3	29.3
Acrysol I-62 (1)	60	49.7	49.7	49.8
D/DI water	137	137.3	137.3	141.7
CG6	-	8.78	8.78	-
Brij 78	-	1.46	-	-
Compound 4	-	-	1.46	4.34
Test Results				
Transparency	4	10	10	10
Color development	5	10	10	'12'

What is claimed is:

1. An aqueous dispersion comprising a solid and a dispersing agent for said solid, said dispersing agent having the following formula:

$$Y.O_2C.(HR)C.C.(HR^1).CO_2.(C_mH_{2m}O)_n.R^2$$

wherein

one of R and R^1 is C_{14} to C_{22} alkyl or alkenyl and the other is hydrogen;

n is from about 4 to about 200 (and as it is an average, it may be non-integral);

m is 2, 3 or 4 (and may vary along the polyoxyalkylene chain);

R^2 is hydrogen (H) or C_1 to C_{22} hydrocarbyl; and

Y is H, a metal, a C_1 to C_{22} hydrocarbyl group, or a group of the formula $(C_mH_{2m}O)_n.R^2$, wherein m, n and R^2 are independently as defined above.

2. The dispersion of claim 1 wherein the dispersing agent is of the following formula:

$$Y.O_2C.(HR)C.C(HR^1).CO_2.(C_mH_{2m}O)_n.R^2$$

3. The dispersion of claim 1 wherein R or R^1 is C_{18}, n is 114 and R^2 is methyl.

4. The dispersion of claim 1 wherein R or R^1 is C_{18}, and n is 110.

5. The dispersion of claim 1 wherein R or R^1 is C_{18}, and n is 182.

6. The dispersion of claim 1 wherein R or R^1 is C_{18}, n is 45, R^2 is methyl, and Y is H or methyl.

7. The dispersion of claim 1 wherein R or R^1 is C_{18} and n is 45.

8. The dispersion of claim 1 wherein R or R^1 is C_{14} and n is 12 or 22.

9. The dispersion of claim 1 wherein R or R^1 is C_{18} and n is 22.

10. The dispersion of claim 1 wherein R or R^1 is C_{14} and n is 34.

11. The dispersion of claim 1 wherein R or R^1 is C_{16} and n is 34.

12. The dispersion of claim 1 wherein R or R^1 is C_{18} and n is 34.

13. The dispersion of claim 1 wherein R or R^1 is C_{14} and n is 4.

14. The dispersion of claim 1 wherein R or R^1 is C_{14} and n is 8.

15. The dispersion of claim 1 wherein R or R^1 is C_{18} and n is 8.

16. The dispersion of claim 1 wherein R or R^1 is C_{18}, n is 45, R_2 is methyl, and Y is butyl.

17. The dispersion of claim 1 wherein the solid is a pigment or a dyestuff.

18. The dispersion of claim 17 wherein the pigment is an inorganic or organic compound.

19. The dispersion of claim 18 wherein the pigment is an inorganic compound selected from the group consisting of carbon black, titanium dioxide and iron oxide.

20. The dispersion of claim 18 wherein the pigment is an organic compound selected from the group consisting of phthalocyanine blue and phthalocyanine green.

21. The dispersion of claim 1 wherein the amount of the dispersing agent ranges from about 0.3% to about 40% based on the weight of the solid.

22. The dispersion of claim 1 wherein the amount of the dispersing agent ranges from about 0.5% to about 25%.

23. The dispersion of claim 21 wherein the solid is present in an amount of from about 10% to about 80% based on the total weight of the dispersion.

24. The dispersion of claim 23 wherein the solid is present in an amount of from about 20% to about 65%.

25. The dispersion of claim 1 which further comprises a water-soluble or water-insoluble resin.

26. The dispersion of claim 25 wherein the resin is water-insoluble.

27. The dispersion of claim 26 wherein the water-insoluble resin is selected from the group consisting of acrylic, styrene-acrylic, polyester, polyurethane, and acrylic-polyurethane.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 97/07704

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09B67/46 C09D17/00 B01F17/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09B C09D B01F C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 074 619 A (HOECHST AG) 23 March 1983 see the whole document ---	1-27
Y	EP 0 628 612 A (LUBRIZOL CORP) 14 December 1994 see the whole document ---	1-27
Y	WO 94 00508 A (ICI PLC ;CARPENTER NEIL MICHAEL (GB); MCGREGOR GORDON (GB); WILNE) 6 January 1994 cited in the application see abstract see page 9, line 21 - line 22 ---	1-27
Y	EP 0 064 225 A (HOECHST AG) 10 November 1982 see abstract see page 9, line 26 - line 27 ---	1-27
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 August 1997	10.09.97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	**Authorized officer** Dauksch, H

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INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 97/07704

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO 96 16930 A (ICI PLC ;ANDERSON STEVEN JOHN (GB); CARPENTER NEIL MICHAEL (GB)) 6 June 1996 see the whole document	1-27
A	WO 95 06096 A (ICI PLC ;MOTSON HAROLD RUSSELL (GB)) 2 March 1995 see the whole document	1-27
A	EP 0 032 289 A (CHINOIN GYOGYSZER ES VEGYESZET) 22 July 1981 see abstract	1-27
A	GB 2 001 083 A (ICI LTD) 24 January 1979 cited in the application see abstract	1
A	EP 0 208 041 A (ICI PLC) 14 January 1987 cited in the application see abstract	1

1

Form PCT/ISA/218 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

...ormation on patent family members

Intern ...al Application No
PCT/US 97/07704

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0074619 A	23-03-83	DE 3136213 A	31-03-83
		BR 8205322 A	23-08-83
		US 4440902 A	03-04-84
EP 0628612 A	14-12-94	AU 666441 B	08-02-96
		AU 6316394 A	01-12-94
		CA 2124156 A	26-11-94
		JP 7008791 A	13-01-95
WO 9400508 A	06-01-94	AU 679918 B	17-07-97
		AU 4350593 A	24-01-94
		CZ 9403280 A	14-06-95
		EP 0647248 A	12-04-95
		FI 946075 A	23-12-94
		HU 68780 A	28-07-95
		JP 7508546 T	21-09-95
		NZ 253297 A	24-02-97
		SK 159694 A	07-06-95
		ZA 9304479 A	22-03-95
EP 0064225 A	10-11-82	DE 3116581 A	30-12-82
		JP 57182360 A	10-11-82
		US 4389213 A	21-06-83
WO 9616930 A	06-06-96	AU 3986795 A	19-06-96
WO 9506096 A	02-03-95	AU 7390594 A	21-03-95
		CA 2170134 A	02-03-95
		EP 0715646 A	12-06-96
		JP 9501726 T	18-02-97
		ZA 9406271 A	20-03-95
EP 0032289 A	22-07-81	EP 0107199 A	02-05-84
		US 4395568 A	26-07-83
GB 2001083 A	24-01-79	AU 518818 B	22-10-81
		AU 3780278 A	10-01-80
		BE 868890 A	10-01-79
		CA 1117689 A	02-02-82
		CH 640150 A	30-12-83

INTERNATIONAL SEARCH REPORT

...ormation on patent family members

Intern al Application No
PCT/US 97/07704

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2001083 A		DE 2830860 A	01-02-79
		FR 2397226 A	09-02-79
		JP 1570685 C	25-07-90
		JP 54037082 A	19-03-79
		JP 63030057 B	16-06-88
		NL 7807584 A,C	17-01-79
		US 4224212 A	23-09-80
EP 0208041 A	14-01-87	AU 585924 B	29-06-89
		AU 5185086 A	31-07-86
		BR 8600192 A	30-09-86
		CA 1270850 A	26-06-90
		JP 6067463 B	31-08-94
		JP 61174939 A	06-08-86
		US 4861380 A	29-08-89

97-549702/50 A97 E19 F06 G02 (A25 E23 E36) **ICIL 96.05.02**

ICI AMERICAS INC *WO 9741178-A1

96.05.02 96US-016716 *(97.11.06)* C09B 67/46, B01F 17/44, C09D 17/00

Aqueous dispersion used in manufacturing paints and inks - contains substituted succinic anhydride derivatives as dispersing agent provides high pigment or dyestuff content dispersions with good fluidity and high stability (Eng)

C97-175341 N(AU BR CA CN IL JP KR MX NZ) R(AT BE CH DE DK ES FI FR GB GR IE IT LU MC NL PT SE)

Addnl. Data: BOUVY A, CARPENTER N M, HIBBERT P G

97.04.23 97WO-US07704

A(8-E1, 8-M1A) E(10-E4K, 25) F(3-C6, 3-F27) G(2-A3, 2-A4A)

An aqueous dispersion comprises a solid, and a dispersing agent of formula (I)

$$Y.O_2C.(HR)C.C.(HR^1).CO_2.(C_mH_{2m}O)_n.R^2 \quad (I)$$

one of R or R^1 = 14 - 22C alkyl or alkenyl, while the other = H;
n = 4 - 200;
m = 2, 3, 4 and may vary along the polyoxyalkylene chain;
R^2 = H or 1 - 22C hydrocarbyl; and

Y = H, metal, 1 - 22C hydrocarbyl or $(C_mH_{2m}O)_n.R^2$.

MORE SPECIFICALLY

When R or R^1 = 18C, n = 8, 22, 34, 45, 110 or 182, R^2 = methyl, and Y = H, methyl or butyl; When R or R^1 = 16C, n = 34; and when R or R^1 = 14C, n = 4, 8, 12, 22 or 34

USE

The dispersing agent is useful in producing pigment and dyestuff dispersions. The pigment dispersions are useful in manufacturing printing inks, particularly publication gravure and newsprint inks, paints and coatings. The dyestuff dispersions are useful in preparing textile printing inks or solvent dyeing systems, particularly where the dyestuff is a sublimable disperse dyestuff for transfer printing.

ADVANTAGE

The dispersing agents are readily made with low odour. The invention allows the preparation of high pigment content mill-bases with good fluidity and high stability which can be used in preparing

Dewent

superior paints and inks with good durability, gloss and moisture and foam resistance. The dispersing agent does not have an adverse effect on the performance of the paint or ink, unlike water-soluble resins.

The dispersion has improved wetting properties, reduced tendency to foam which makes milling and handling more convenient and reduces or eliminates the need for antifoams which have a deleterious effect on paint or ink performance in the mill-base, and reduces or eliminates the need for water-soluble resins which have an adverse effect on durability and/or moisture resistance.

PREFERRED MATERIALS

The solid is a pigment or a dyestuff. The pigment is an inorganic compound, preferably carbon black, titanium dioxide or iron oxide, or an organic compound, preferably phthalocyanine blue or phthalocyanine green. The dispersion may further comprise a water-soluble or water-insoluble resin, preferably a water-insoluble resin selected from acrylic, styrene-acrylic, polyester, polyurethane and acrylic-polyurethane.

PREFERRED COMPOSITION

The dispersing agent comprises 0.3 - 40 (0.5 - 25) wt.%, based on the weight of the solid. The solid comprises 10 - 80 (20 - 65) wt.% of the dispersion.

EXAMPLE

(I) wherein R or R^1 = 18C alkenyl, R^2 = methyl, Y = methyl, n = 45 and m = 2, was added to a 250 ml glass bottle. Demineralised water and n-hexanol were added and the components gently mixed to dissolve the dispersing agent. 3 mm diameter glass beads were added (1/2 of the mill-base). "TIOXIDE TR-92" (RTM: white R2, rutile 94% TiO_2, Al, Zr coated + organic treatment) pigment was added and a dispersion prepared by shaking for 0.5 hr.

Using 0.5 wt.% (I) at pH 7 viscosity of a 65 wt.% dispersion was 9800 mPa.s, using 0.8 wt.% (I) it was 7000 mPa.s and using 1.1 wt.% (I) it was 6240 mPa.s. At pH 10.2, the corresponding viscosities were 1340, 1220 and 1470 mPa.s respectively. (CG)

(29pp2262DwgNo.0/0)

SR:EP208041 EP32289 EP628612 EP64225 EP74619 GB2001083 WO9400508 WO9506096 WO9616930